

What Is Claimed Is:

1. A process for producing polyimide aerogels comprising:  
contacting a diamine monomer and an aromatic dianhydride monomer in a solvent under conditions conducive to formation of a poly(amic acid);  
contacting the poly(amic acid) in a first solvent with a dehydrating agent to form a polyimide gel by imidization; and  
drying the polyimide gel in the presence of supercritical CO<sub>2</sub> to afford an polyimide aerogel.
2. The process of claim 1 in which the first solvent is not miscible with supercritical CO<sub>2</sub>, the method further comprises the step of exchanging the first solvent with a second solvent which is miscible with supercritical CO<sub>2</sub> prior to drying the polyimide gel.
3. The process of claim 1 in which the process further comprises post-curing the polyimide aerogel at a temperature of between about 50°C and about 450°C before or after supercritical CO<sub>2</sub> drying.
4. The process of claim 1, wherein the diamine monomer is an aliphatic diamine, an aromatic diamine, a bis( $\omega$ -aminoalkyl)terminated polysiloxane or a combination thereof.
5. The process of claim 1, wherein the diamine monomer comprises an aromatic monomer having two or more amine groups.
6. The process of claim 5, wherein the aromatic diamine monomer comprises a diamine monomer and may further comprise one or more aromatic triamine monomers or aromatic tetraamine monomers.

7. The process of claim 1, wherein the aromatic dianhydride is selected from pyromellitic dianhydride, 3, 3' 4, 4'-biphenyltetracarboxylic dianhydride, 3, 3' 4, 4'-benzophenone tetracarboxylic dianhydride, and 2,3,6,7-naphthylene tetracarboxylic acid dianhydride.

8. The process of claim 1, wherein the dehydrating agent is a chemical dehydrating agent.

9. The process of claim 8, wherein the dehydrating agent is a mixture of an alkanedioic anhydride and an organic base selected from optionally substituted pyridines and optionally substituted trialkyl amines.

10. The process of claim 1, wherein the product polyimide aerogel has surface area in excess of 500 m<sup>2</sup>/g, a mesoporous pore size of between about 5 nm and about 100 nm, and a narrow pore size distribution.

11. The process of claim 1, wherein the product polyimide aerogel has surface area in excess of 1000 m<sup>2</sup>/g, a mesoporous pore size of between about 5 nm and about 100 nm, and a narrow pore size distribution.

12. A process of producing carbon aerogels comprising the steps of providing a polyimide aerogel; and pyrolyzing the polyimide aerogel under in an inert atmosphere to form a carbon aerogel.

13. A process of producing a carbon aerogel comprising the steps of contacting a diamine monomer and an aromatic dianhydride monomer in a solvent under conditions conducive to formation of a poly(amic acid); contacting the poly(amic acid) in a solvent with a dehydrating agent to form a polyimide by imidization;

drying the polyimide gel in the presence of supercritical CO<sub>2</sub> to afford an polyimide aerogel; and

pyrolyzing the polyimide aerogel under in an inert atmosphere to form a carbon aerogel.

14. The process of claim 13 in which the first solvent is not miscible with supercritical CO<sub>2</sub>, the method further comprises the step of exchanging the first solvent with a second solvent which is miscible with supercritical CO<sub>2</sub> prior to drying the polyimide gel.

15. The process of claim 13 in which the process further comprises post-curing the polyimide aerogel at a temperature of between about 50°C and about 450°C before or after supercritical CO<sub>2</sub> drying.

16. The process of claim 13, wherein the diamine monomer is an aliphatic diamine, an aromatic diamine, a bis( $\omega$ -aminoalkyl)terminated polysiloxane, or a combination thereof.

17. The process of claim 16, wherein the diamine monomer comprises an aromatic diamine monomer and may further comprise one or more aromatic triamine monomers or aromatic tetraamine monomers.

18. The process of claim 13, wherein the aromatic dianhydride is selected from optionally substituted pyromellitic dianhydride, optionally substituted 3,3',4,4'-biphenyltetracarboxylic dianhydride, optionally substituted 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and optionally substituted 2,3,6,7-naphthylene tetracarboxylic acid dianhydride.

19. The process of claim 13, wherein the dehydrating agent is a chemical dehydrating agent.

20. The process of claim 19, wherein the dehydrating agent is a mixture of an alkanedioic anhydride and an organic base selected from optionally substituted pyridines and optionally substituted trialkyl amines.

21. The process of claim 13, wherein the product carbon aerogel has surface area in excess of 400 m<sup>2</sup>/g, a mesoporous pore size of between about 5 nm and about 100 nm, and a narrow pore size distribution.

22. The process of claim 13, wherein the product carbon aerogel has surface area between about 500 m<sup>2</sup>/g and about 1200 m<sup>2</sup>/g, a mesoporous pore size of between about 5 nm and about 100 nm, and a narrow pore size distribution.

23. The process of claim 13, wherein the carbon aerogel further comprises between about 0.01% and about 15% nitrogen by weight.

24. The process of claim 23, wherein the composition of the carbon aerogel comprises up to about 9% nitrogen by weight at a pyrolysis temperature of 700°C or up to about 6.5% nitrogen by weight at a pyrolysis temperature of 900°C.

25. A process for producing carbon aerogels impregnated with dispersed metal particles comprising:

contacting a diamine monomer and an aromatic dianhydride monomer in a solvent under conditions conducive to formation of a poly(amic acid);

dissolving a soluble metal ion salt and the poly(amic acid) in a solvent;

contacting the solution of poly(amic acid) and soluble metal ion salt with a dehydrating agent to form a polyimide gel by imidization of the poly(amic acid);

drying the polyimide gel in the presence of supercritical CO<sub>2</sub> to afford an polyimide aerogel; and

pyrolyzing the derived aerogel under protection of an inert atmosphere to form the carbon aerogel having highly dispersed transition metal particles.

26. A process for producing carbon xerogel-aerogel hybrid impregnated with highly dispersed metal particles, the process comprising the steps of:

contacting a diamine monomer and an aromatic dianhydride monomer in a solvent under conditions conducive to formation of a poly(amic acid);  
dissolving a soluble metal salt and the poly(amic acid) in a solvent;  
contacting the solution of poly(amic acid) and soluble metal ion salt with a dehydrating agent to form a polyimide gel by imidization of the poly(amic acid);  
precipitating at least a portion of the soluble metal salt onto the polyimide gel;  
drying the polyimide gel in the presence of supercritical CO<sub>2</sub> to afford an polyimide aerogel; and

pyrolyzing the derived aerogel under protection of an inert atmosphere to form the carbon xerogel-aerogel having highly dispersed transition metal particles.

27. A process for producing a metal carbide aerogel, a metal carbide-carbon aerogel or carbon aerogel impregnated with highly dispersed metal particles, the process comprising the steps of:

contacting a diamine monomer and an aromatic dianhydride monomer in a solvent under conditions conducive to formation of a poly(amic acid);  
preparing a solution of a soluble metal ion salt, an epoxide compound and the poly(amic acid) in a solvent such that a molar ratio of epoxide compound to the metal ion is between about 1 to about 8;

contacting the solution of poly(amic acid) , an epoxide compound and soluble metal ion salt with a dehydrating agent to form a polyimide gel by imidization of the poly(amic acid);

drying the polyimide gel in the presence of supercritical CO<sub>2</sub> to afford an polyimide aerogel; and

pyrolyzing the derived aerogel under protection of an inert atmosphere to form the aerogel having highly dispersed transition metal particles.

28. The process of any one of claims 25 through 27 in which the first solvent is not miscible with supercritical CO<sub>2</sub>, the method further comprises the step of

exchanging the first solvent with a second solvent which is miscible with supercritical CO<sub>2</sub> prior to drying the polyimide gel.

29. The process of any one of claims 25 through 27, wherein the metal is selected from the group consisting of Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Cu, Ag, Zn, Si, Sn, Pb, Sb, Nb, Bi, Hf, Ba, Al, B, P, As and combinations thereof.

30. The process of claim 27, wherein the epoxide is a 1,2-epoxyalkane having from 2 to about 12 carbon atoms.

31. The process of claim 27, wherein the epoxide is selected from the group of 1,2-epoxybutane and 1,2-epoxypropane

32. The process of claim 27, wherein the epoxide compound is added to the reaction as an admixture with deionized water and wherein the epoxide compound is added to the reaction after gelation of the polyimide.

33. The process of claim 27, wherein the ratio of epoxide to metal ion is at range of about 1 to about 8.

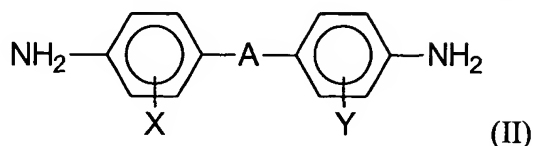
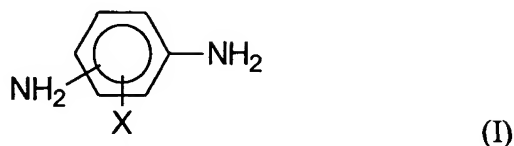
34. The process of claim 27, wherein the ratio of deionized water to epoxide is about 1 to about 4.

35. The process of claim 28, wherein the process further comprises addition of a gelation controlling agent to the poly(amic acid) solution such that a molar ratio of gelation controlling agent to metal ion is between about 1 and about 8.

36. The process of claim 35, wherein the molar ratio of gelation controlling agent to metal ion is between about 1 and about 4.

37. The process of claim 35, wherein the gelation controlling agent is an optionally substituted acetoacetate or an optionally substituted alkyl acetoacetate.
38. The process of claim 35, wherein the gelation controlling agent is selected from the group of 2,4-pentanedione and ethyl acetoacetate.
39. The process of any one of claims 1, 13, or 25-27, wherein a reinforcing agent is added to the polyimide wet gel before drying with supercritical CO<sub>2</sub>.
40. The process of claim 39, wherein the reinforcing agent is selected from a reinforcement pad, organic or inorganic fibers carbon nanotubes, metallic fillers or particles or inorganic fillers or particles.
41. The process of claim 39, wherein the fiber reinforcement pad is selected from a non-woven or woven fiber reinforcement composed of a polymeric organic fiber, a glass fiber, a ceramic fiber, a carbon precursor fiber, or a biopolymer fiber.
42. The process of any one of claims 1, 13, or 25-27, in which the process further comprises a post-curing step, at an elevated temperature, to induce substantially complete imidization, wherein the post curing step is conducted:
- (a) prior to the solvent removal step wherein the post-curing step is conducted under a pressure of about 20 psi to about 4000 psi; or
  - (b) after the solvent removal step, wherein the post-curing step is conducted under an inert atmosphere or in a vacuum at a temperature of between about 50°C to about 450°C.
43. The process of any one of claims 1, 13, or 25-27, wherein the diamine monomer is represented by the formula H<sub>2</sub>N-X-NH<sub>2</sub>, wherein X represents a difunctional aliphatic hydrocarbon group, an amino-terminated polysiloxane, a difunctional aromatic hydrocarbon group, or difunctional heteroaromatic group which may be optionally substituted.

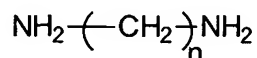
44. The process of claim 43, wherein the aromatic diamine is represented by either formula (I) and (II)



wherein X and Y are monofunctional substituents selected from hydrogen, halogen, carboxyl, lower alkyl and lower alkoxy groups, X and Y may be the same or different substituents and A is a bivalent connecting group selected from -O-, -S-, -CO-, -S-, -SO<sub>2</sub>-, and -CH<sub>2</sub>-, or A is a single bond; wherein alkyl or alkoxy contains 1 to 4 carbon atoms.

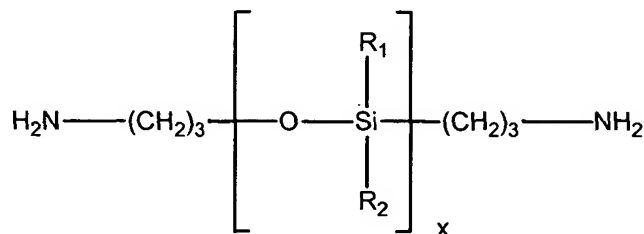
45. The process of claim 44, wherein the aromatic diamine is 1,4-phenylenediamine or 4,4'-diamino-biphenyl.

46. The process of claim 43, wherein the diamine monomer is an aliphatic diamine containing a linear alkyl chain unit of formula.



wherein n is a integer number from 1 to 12.

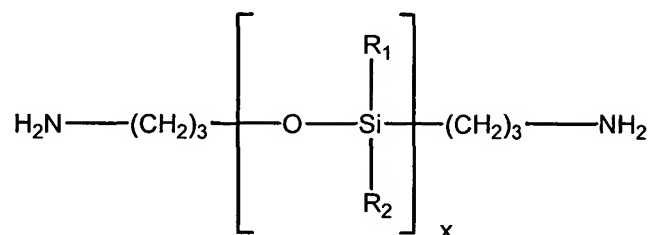
47. The process of claim 43, wherein the diamine monomer is an amino terminated polysiloxane of the formula





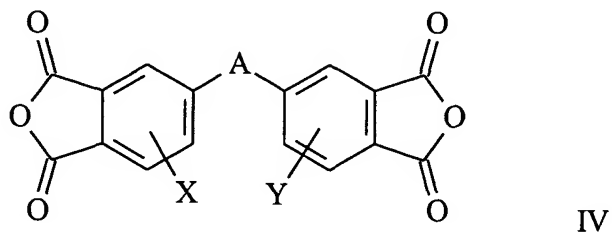
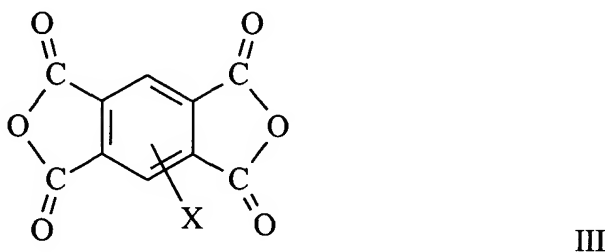
wherein R<sub>1</sub> and R<sub>2</sub> are each independently selected from the group consisting of hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted cycloalkyl-alkyl, optionally substituted aryl, optionally substituted aralkyl, and optionally substituted alkoxy.

48. The process of claim 47, wherein the amino terminated polysiloxane is a thermally stable polysiloxane of the formula



wherein R<sub>1</sub> and R<sub>2</sub> are independently selected from optionally substituted alkyl having from 1 to about 12 carbon atoms and optionally substituted phenyl.

49. The process of any one of claims 1, 13, or 25-26, wherein the aromatic dianhydride is monomer represented by either formula III or IV



wherein X and Y are monofunctional substituents selected from hydrogen, halogen, carboxyl, alkyl, and alkoxy groups, X and Y may be the same or different substituents and A is a bivalent connecting group selected from -O-, -S-, -CO-, -S-, -SO<sub>2</sub>-, -CH<sub>2</sub>-, or A is a single bond.

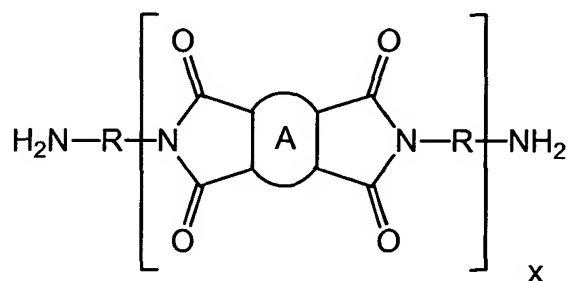
50. The process of claim 49, wherein the aromatic dianhydride is selected from the group consisting of optionally substituted pyromellitic dianhydride, optionally substituted 3,3',4,4'-biphenyltetracarboxylic dianhydride, optionally substituted 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and optionally substituted 2,3,6,7-naphthylene tetracarboxylic acid dianhydride.

51. The process of any one of claims 1, 13, or 25-27, wherein the dehydrating agent comprises at least one compound selected from the group consisting of acetic anhydride, propionic anhydride, n-butyric anhydride, benzoic anhydride, trifluoroacetic anhydride, and phosphorus trichloride.

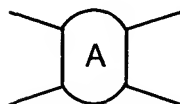
52. The process of claim 43, wherein the organic base is selected from optionally substituted mono-, di- and trialkylamines, optionally substituted pyridines, optionally substituted isoquinoline, optionally substituted morpholine, optionally substituted piperidine, and optionally substituted piperazine.

53. A polyimide aerogel comprising at least one polyimide polymer.

54. A polyimide aerogel of claim 53 wherein at least one polyimide polymer is a polyimide of the formula:



wherein



represents an optionally substituted aryl group, an optionally substituted alicyclic group, an optionally substituted heteroaryl group, or an optionally substituted heteroalicyclic group;

R is an optionally substituted difunctional aryl, difunctional optionally substituted alkylene, optionally substituted difunctional alicyclic hydrocarbon group, an optionally substituted difunctional heteroaryl or a combination thereof; and

x is a number greater than about 2.

55. A polyimide aerogel prepared by the process of claim 1.

56. A polyimide aerogel of any one of claims 53 through 55, having a density of 0.3 g/cc or less.

57. A polyimide aerogel of claim 56 wherein the aerogel density is between 0.01 and 0.2 g/cc.

58. A polyimide aerogel of claim 53, having a yield strength of about 1 MPa or more.

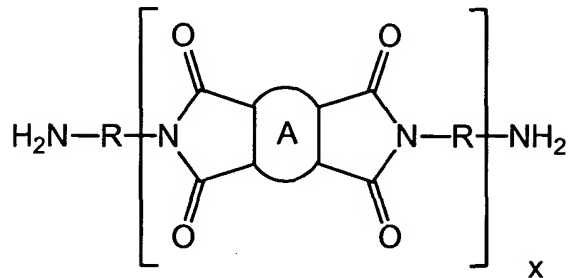
59. A polyimide aerogel of any one of claims 53 through 55, having a surface area of more than about 400 m<sup>2</sup>/g.

60. A polyimide aerogel of claim 59 having a surface area of between about 500 and about 1200 m<sup>2</sup>/g.

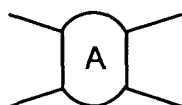
61. A polyimide aerogel of claim 53 having an average pore size of between about 1 to about 100 nm.

62. A polyimide aerogel of claim 61 having an average pore size of between about 10 and 40 nm.

63. A polyimide aerogel of claim 54 according to the formula



wherein

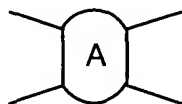


represents an optionally substituted aryl group, an optionally substituted alicyclic group, an optionally substituted heteroaryl group, or an optionally substituted heteroalicyclic group;

R is an optionally substituted difunctional aryl, difunctional optionally substituted alkylene, or a combination thereof; and

x is a number greater than about 2.

64. A polyimide aerogel of claim 63, wherein



represents phenyl or biphenyl;

R represents phenyl, biphenyl, C<sub>1-12</sub>alkylene; and

x is a number greater than about 5.

65. A carbon aerogel prepared by the process of any one of claims 12 or 13.

66. A carbon aerogel prepared by pyrolysis of a polyimide aerogel under an inert atmosphere at a temperature of between about 500°C to about 1600 °C.

67. A carbon aerogel comprising carbon and nitrogen wherein the carbon aerogel comprises at least 0.01% nitrogen by weight.
68. The carbon aerogel of claim 67, wherein the carbon aerogel is electrically conductive.
69. A carbon aerogel of claim 67, wherein the carbon aerogel comprises amorphous carbon, microcrystalline carbon, or a combination thereof, and the carbon aerogel having a yield strength of at least 1 MPa.
70. A carbon aerogel of claim 67, wherein the carbon aerogel comprises between about 0.1 and about 15% nitrogen by weight.
71. A carbon aerogel of claim 70, wherein the carbon aerogel comprises between about 2 and about 8% nitrogen by weight.
72. A carbon aerogel of claim 67, having a density of about 1.0 g/cc or less.
73. A carbon aerogel of claim 67, wherein the carbon aerogel density is between about 0.01 and 0.8 g/cc.
74. A carbon aerogel of claim 67, wherein the carbon aerogel has an average pore size of between about 5 nm and about 50 nm.
75. A carbon aerogel of claim 67, wherein the carbon aerogel has a surface area of about 400 m<sup>2</sup>/g or more.
76. A carbon aerogel of claim 75, wherein the carbon aerogel has a surface area of between about 600 m<sup>2</sup>/g and about 1200 m<sup>2</sup>/g.

77. A carbon aerogel of claim 67, wherein the aerogel further comprises metal nanoparticles which are dispersed in the pores of the aerogel.

78. The carbon aerogel of claim 77, wherein the ratio of carbon to metal is between about 1:1 to about 1000:1.

79. The carbon aerogel of claim 78, wherein the metal is selected from the group consisting of Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Cu, Ag, Zn, Si, Sn, Pb, Sb, Nb, Bi, Hf, Ba, Al, B, P, As and combinations thereof.

80. A composite carbon aerogel comprising carbon and at least one metal where the composite aerogel is prepared by the process of any one of claims 25 through 27.

81. A composite metal-carbon aerogel comprising nitrogen doped carbon aerogel domains, metal carbide domains, or a combination thereof.

82. The composite metal-carbon aerogel of claim 81, wherein the composite aerogel comprises interpenetrating networks of a carbon aerogel and a metal carbide aerogel.

83. The composite metal-carbon aerogel of claim 81, wherein the composite aerogel further comprises 0.1 to about 15% nitrogen.

84. A composite metal-carbon aerogel of claim 81, having a yield strength of at least 1 MPa.

85. A composite metal-carbon aerogel of claim 81, wherein the aerogel has an average pore size of between about 5 nm and about 50 nm.

86. A composite metal-carbon aerogel of claim 81, wherein the aerogel has a surface area of about 100 m<sup>2</sup>/g to about 1000 m<sup>2</sup>/g.

87. A composite metal-carbon aerogel of claim 81, wherein the aerogel has a surface area of about 200 m<sup>2</sup>/g to about 600 m<sup>2</sup>/g.

88. The composite metal-carbon aerogel of claim 81, wherein the aerogel has nanoparticles of a second metal dispersed throughout pores of the aerogel where the second metal may be the same or different from the metal of the metal carbide component of the composite aerogel.

89. A composite metal-carbon aerogel of claim 88, wherein the second metal is selected from Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Cu, Ag, Zn, Si, Sn, Pb, Sb, Nb, Bi, Hf, Ba, Al, B, P, As and combinations thereof.

90. A composite metal-carbon aerogel of claim 80, in which the composite aerogel is electrically conductive.

91. A composite metal-carbon aerogel of claim 81, in which the composite aerogel is electrically conductive.

92. A composite metal-carbon aerogel of claim 82, in which the composite aerogel is electrically conductive.

93. A composite metal-carbon aerogel of claim 88, in which the composite aerogel is electrically conductive.

94. A metal carbide aerogel prepared by the process of claim 27.

95. The metal carbide aerogel of claim 94, wherein the composite aerogel further comprises 0.1 to about 15% nitrogen.

96. The metal carbide aerogel of claim 94 in which the metal carbide aerogel is electrically conductive.

97. A metal carbide aerogel of claim 94 having a yield strength of at least 1 MPa.

98. A metal carbide aerogel of claim 94, wherein the aerogel has an average pore size of between about 5 nm and about 50 nm.

99. A metal carbide aerogel of claim 94, wherein the aerogel has a surface area of about 200 m<sup>2</sup>/g or more.

100. A metal carbide aerogel of claim 99, wherein the aerogel has a surface area of between about 200 m<sup>2</sup>/g and about 1000 m<sup>2</sup>/g.

101. The metal carbide aerogel of claim 94, wherein the aerogel has nanoparticles of a second metal dispersed throughout pores of the aerogel where the second metal may be the same or different from the metal of the metal carbide component of the composite aerogel.

102. A composite metal-carbon aerogel of claim 101, wherein the second metal is selected from Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Cu, Ag, Zn, Si, Sn, Pb, Sb, Nb, Bi, Hf, Ba, Al, B, P, As and combinations thereof.

103. A xerogel/aerogel hybrid prepared by the process of claim 26.

104. An article of manufacture comprising at least one aerogel selected from polyimide aerogels, carbon aerogels comprising carbon and nitrogen, metal carbide aerogels, hybrid carbon-metal carbide aerogels, each of which may have metal particles dispersed in the pores of the aerogel.



105. The article of manufacture of claim 104, wherein the aerogel is selected from aerogels provided by any one of claims 53, 54, 66, 67, 77, 88, 81, 94 or 101.

106. An electrode composed of at least one aerogel selected from carbon aerogels comprising carbon and nitrogen, metal carbide aerogels, hybrid carbon-metal carbide aerogels, each of which may have metal particles dispersed in the pores of the aerogel.

107. The electrode of claim 106, wherein the aerogel is selected from aerogels provided by any one of claims 66, 67, 77, 88, 81, 94 or 101.

108. An electrochemical cell comprising one or more electrodes composed of at least one aerogel selected from carbon aerogels comprising carbon and nitrogen, metal carbide aerogels, hybrid carbon-metal carbide aerogels, each of which may have metal particles dispersed in the pores of the aerogel.

109. The electrochemical cell of claim 108, wherein the aerogel is selected from aerogels provided by any one of claims 66, 67, 77, 88, 81, 94 or 101.

110. An electrochemical cell of claim 108, wherein the electrochemical cell is selected from a battery, a capacitor, a supercapacitor, fuel cell, or capacitive deionization cell.

111. A supported metal catalyst comprising a carbon, metal carbide, or a composite carbon-metal carbide aerogel having metal particles dispersed therein or a metal carbide aerogel.